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Improved Synthesis of 3,5-Diamino-2, 4,6-Trinitrotoluene

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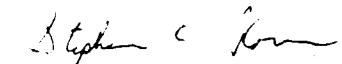
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PREFACE

This report describes the results of work performed by personnel at the Department of Chemistry, University of North Texas, NT Station, Box 5068, Denton, TX 76203-0068, during the period August 1990 through February 1992. The contract program manager was Dr. Alan P. Marchand, and the WL/MNME program manager was Lt Maria E. Boado. Funding was provided by WL/MNME, Eglin AFB FL 32542-5000, under Contract F08635-90-K-0203.

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SECTION 1

INTRODUCTION

Polynitroaromatic compounds constitute an important class of high density energetic materials that are utilized as explosives. Polynitroaromatic compounds that contain an α -C-H group (e.g., 2,4,6-trinitrotoluene, TNT) consistently show greater impact sensitivity than similar compounds that contain the same oxygen balance but do not possess the α -C-H functionality (References 1 and 2). It has been demonstrated that the impact sensitivity of polynitrotoluenes can be reduced significantly by the introduction of one or more amino groups (Reference 3). 3,5-Diamino-2,4,6-trinitrotoluene (DATNT, 1) is of particular interest in this connection, as this compound is proposed to be a more powerful explosive than TNT but is less impact-sensitive (Reference 4). Herein, a three-step, efficient synthesis is described that provides DATNT in 58 percent overall yield from orcinol monohydrate.

SECTION II

DISCUSSION

DATNT has been synthesized previously in two steps by starting with 3,5-dichloro- (Reference 4) or 3,5-dibromotoluene (References 5 and 6). See Figure 1, **2a** or **2b**, respectively. These syntheses suffer from the following limitations:

- o One of the starting materials, **2a**, is not available commercially; the other is available and can be purchased but is very expensive.
- o Due to the cumulative ring-deactivating influence of the halogen substituents, harsh conditions (e.g., fuming nitric acid-concentrated sulfuric acid) are required to effect trinitration of **2a** and **2b**.
- o The reaction of **3b** with ethanolic ammonia has been reported (Reference 6) to require elevated pressure; thus, this reaction must be performed in a sealed reaction vessel.

More recently, Atkins and coworkers (Reference 7) have reported that DATNT can be synthesized by reacting either pentanitrotoluene or 3-amino-2,4,5,6-tetranitrotoluene with ammonia in dioxane at ambient temperature and atmospheric pressure. However, these procedures employ starting materials that are powerful explosives not readily available and must be prepared via multistep syntheses.

In an effort to overcome the limitations described above, a simple and convenient three-step procedure has been developed that affords DATNT in 58 percent overall yield. The procedure employs as starting material 3,5-dihydroxytoluene (orcinol, **2c**), which is both commercially available (as the monohydrate) and relatively inexpensive.

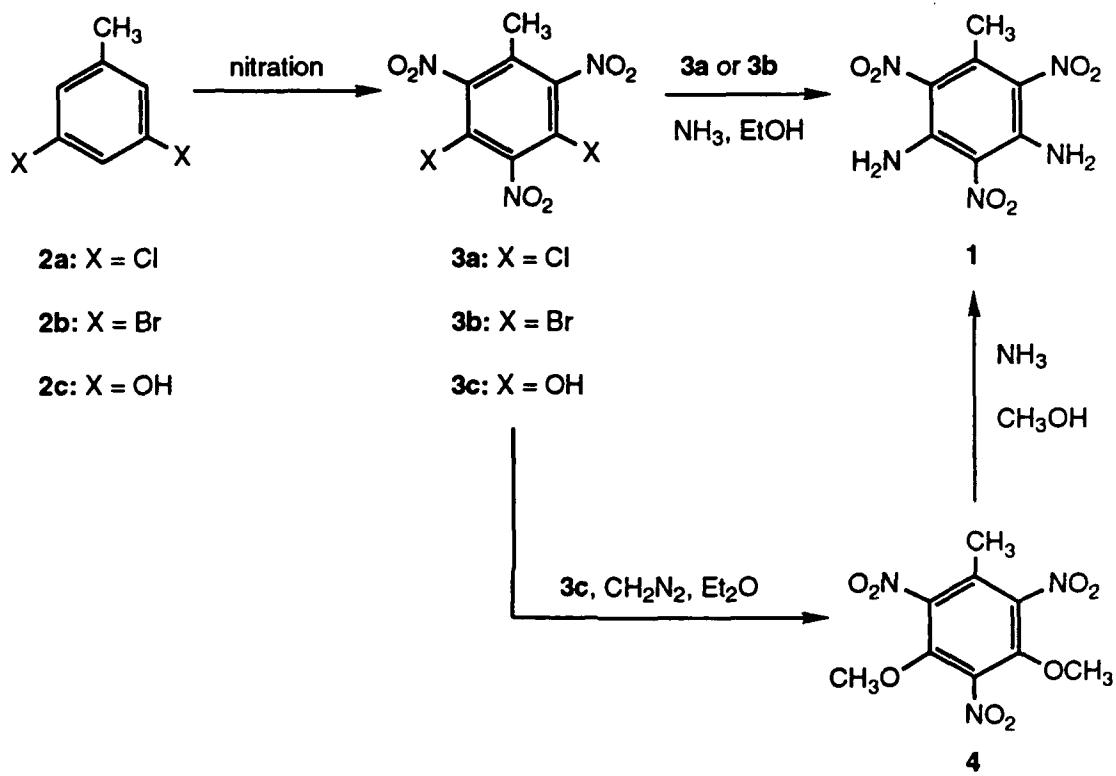


Figure 1. Approaches to the Rational Synthesis of DATNT

The hydroxy groups in **2c** activate the aromatic ring toward electrophilic nitration. Thus, trinitration of this material is performed conveniently and in high yield (77 percent) simply by using concentrated nitric acid-concentrated sulfuric acid (Reference 8). *O*-methylation of the hydroxy groups in the trinitration product, **3c**, is carried out in high yield (94 percent) by using ethereal diazomethane (Reference 9). Finally, nucleophilic aromatic substitution of the methoxy groups in **4** is executed conveniently and in high yield (80 percent) by reacting a methanol solution of this compound with ammonia gas under ambient conditions.

Alternative methods to replace the use of diazomethane for *O*-methylation of **3c** were sought, as diazomethane was regarded as being unsuitable for use in large-scale reactions. The following methods were attempted: (a) dimethyl sulphate, acetone, solid K_2CO_3 , reflux 4 hours; (b) CH_3I , HMPA, aqueous $NaOH$, 25 °C, stir 6 hours; and (c) CH_3I , DMSO, powdered KOH, 25 °C, stir 30 minutes. In each case, decomposition of the starting material resulted; no **4** could be isolated from any of these alternative procedures for performing *O*-methylation of **3c**.

SECTION III

EXPERIMENTAL

Melting points are uncorrected. **WARNING!** Polynitroaromatics are powerful explosives and should be handled with extreme caution.

1. 3,5-DIHYDROXY-2,4,6-TRINITROTOLUENE (3c)

A solution of orcinol monohydrate (**2c**, 284 mg, 2.0 mmol) in concentrated H₂SO₄ (15 mL) is cooled externally (ice-water bath) to 0 °C. A precooled (0 °C) mixture of concentrated HNO₃ (0.8 mL) and concentrated H₂SO₄ (1.6 mL) is added dropwise with stirring to the reaction vessel. This is followed by dropwise addition of cold, concentrated HNO₃ (1.5 mL) to the stirred reaction mixture. The external cold bath is removed, and the reaction mixture is allowed to warm gradually to room temperature during 1 hour. The reaction mixture then is poured into ice water (25 mL). The product, which precipitates immediately, is isolated via suction filtration and air-dried. Pure **3c** (398 mg, 77 percent) is thereby obtained as a yellow-orange microcrystalline solid: mp 166-168 °C (literature mp 171-172 °C [Reference 8]; 162 °C [Reference 10]); IR (nujol) 3160 (s), 1628 (m), 1592 (s), 1541 (s), 1469 (s), 1375 (s), 1188 cm⁻¹ (s); ¹H NMR (acetone-d₆) δ 2.36 (s, 3 H), 10.06 (br s, 2 H); ¹³C NMR (acetone-d₆) δ 14.02 (q), 125.77 (s), 133.64 (s), 134.99 (s), 149.75 (s).

2. 3,5-DIMETHOXY-2,4,6-TRINITROTOLUENE (4)

A solution of diazomethane in diethyl ether is added dropwise with stirring to a solution of **3c** (130 mg, 0.50 mmol) in ethyl acetate (10 mL) (Reference 9). The addition is continued until the yellow color of diazomethane persists, thereby indicating the presence of a slight excess of this reagent. The resulting solution is stirred overnight (15 hours) at room temperature and then is concentrated in vacuo. Pure **4** (135 mg, 94 percent) is thereby obtained as a yellow

microcrystalline solid: mp 66-67 °C (literature [Reference 9] mp 65-66 °C); IR (nujol) 1592 (s), 1538 (s), 1466 (s), 1365 (s), 1136 cm⁻¹ (s); ¹H NMR (CDCl₃) δ 2.26 (s, 3 H), 3.99 (s, 6 H); ¹³C NMR (CDCl₃) δ 13.25 (1), 64.56 (q), 127.63 (s), 138.55 (s), 141.54 (s), 146.19 (s).

3. 3,5-DIAMINO-2,4,6-TRINITROTOLUENE (1)

A solution of **4** (100 mg, 0.35 mmol) in methanol (10 mL) under argon is cooled externally (ice-water bath) to 0 °C and is stirred vigorously. Ammonia gas is bubbled continuously through this cooled solution for 1.5 hours. The external cold bath is removed, and slow passage of ammonia gas through the reaction mixture is continued with vigorous stirring for an additional 1.5 hours. The gas bubbling apparatus is removed, the flask is stoppered, and the reaction mixture is stirred at room temperature for 1.5 hours. The stopper is removed, and excess ammonia is allowed to evaporate slowly from the reaction mixture. During this time, DATNT slowly crystallizes from the reaction mixture. The product is collected by suction filtration, and the residue is washed with methanol and then is air-dried. Pure DATNT (72 mg, 80.4 percent) is thereby obtained as yellow needles: mp 223-224 °C (literature mp 222 °C [Reference 4], 222.5-224 °C [Reference 7]); IR (nujol) 3439 (m), 3320 (m), 1585 (m), 1469 (s), 1340 cm⁻¹ (m); ¹H NMR (CDCl₃) δ 2.41 (s, 3 H), 8.0-8.3 (br s, 4 H).

SECTION IV

SUMMARY AND CONCLUSIONS

In summary, our three-step synthesis of DATNT, described within this report, offers the following advantages:

- o Each synthetic step is easy to set up, to perform, and to work up.
- o Only inexpensive and readily available reagents are required.
- o Mild conditions are utilized for the trinitration step.
- o Handling of polynitroaromatics is minimized, and the procedure does not subject them to harsh environmental conditions.
- o The use of elevated pressure in the amination step is avoided.
- o The desired material is produced in high overall yield.

It is anticipated that this procedure will lend itself readily to scaleup and thus may find application for large-scale synthesis of DATNT.

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